DIFFERENT MODES OF SURFACE PASSIVATION OF GaAs

_Tarak A. Railkar_*, Ajay P. Malshe, Rajesh Bhide, Shiva Hullavarad and S.V. Bhoraskar

Department of Physics, University of Pune, Pune 411 007, India
*** Conexant Systems Inc., Newport Beach CA 92660**

Contact Information:
Conexant Systems Inc.
4311 Jamboree Road MS: E04-401
Newport Beach CA 92660
Tel; 949-483-7062
Fax: 949-483-7299
E-mail: tarak.railkar@conexant.com

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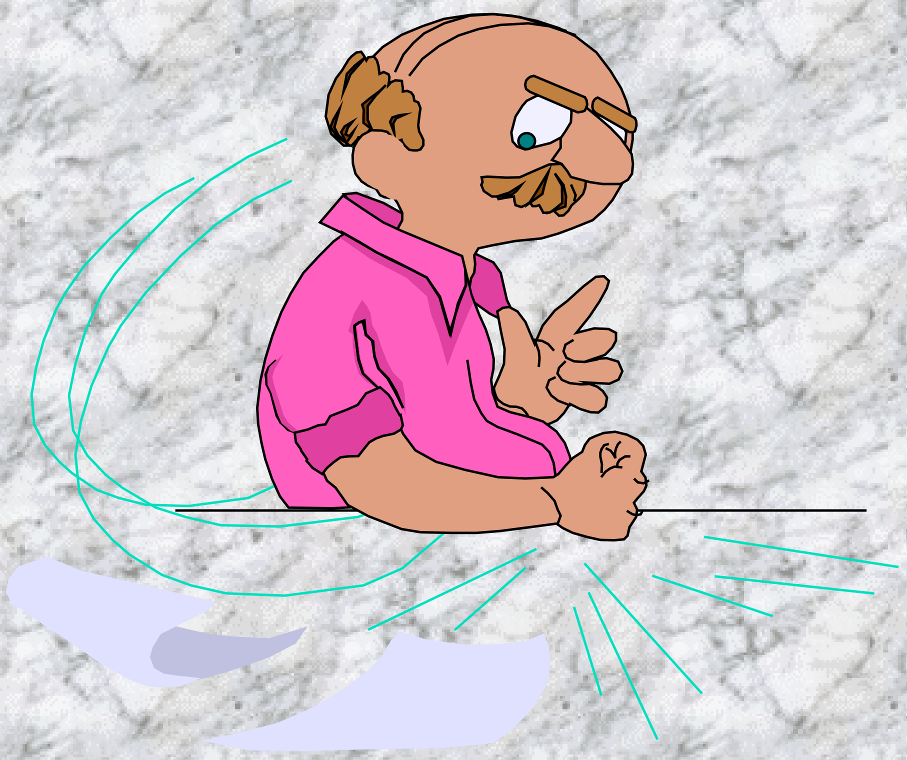
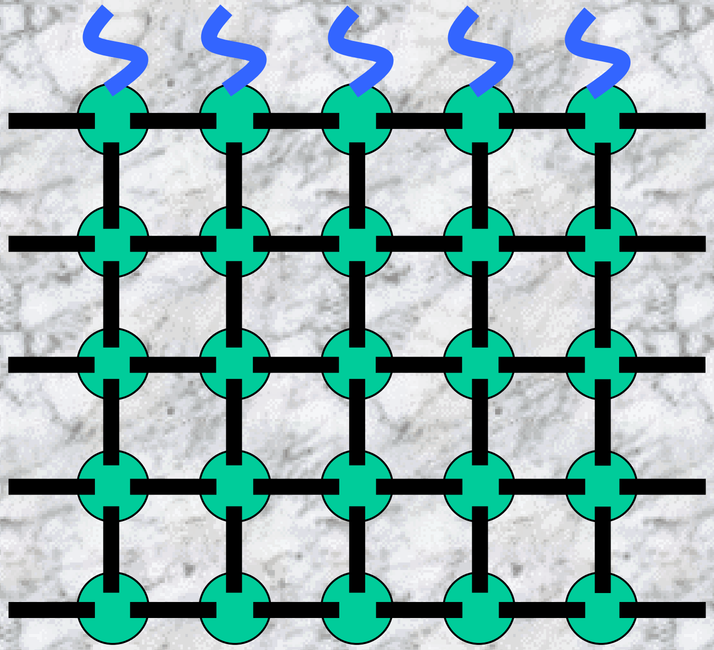
Need for surface passivation

- Protect surface from chemical and/or electronic degradation, due to oxidation
- Reduce density of electronically active surface states

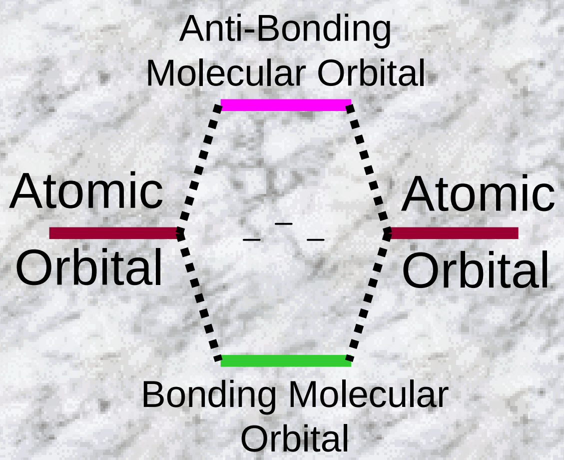


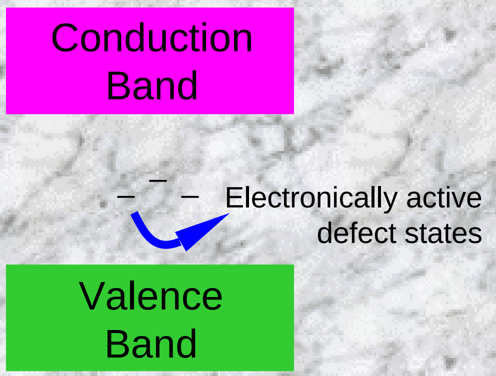
Surface states

Dangling Bonds..



Bulk material



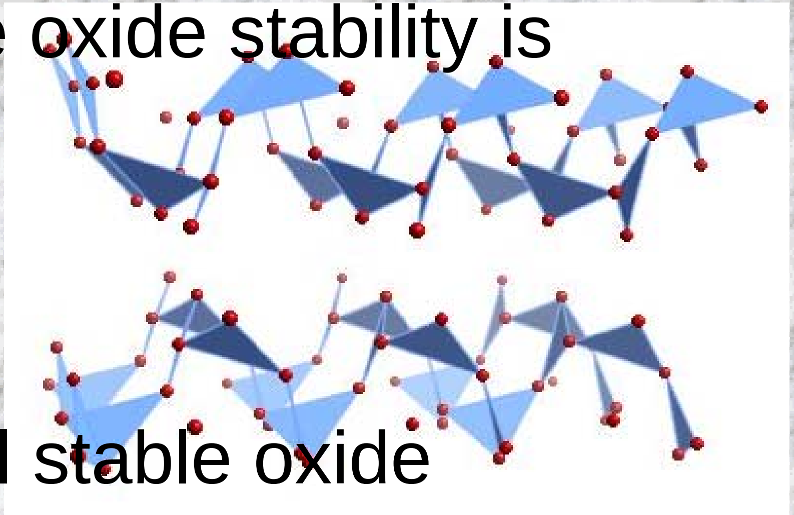


Surface states are electronic states within the semiconductor, caused due to structural effects at the semiconductor surface.

Dangling bonds can generate electronically active defect states, *hence the need for passivation*.

Silicon and GaAs

- Silicon has a natural and stable oxide that passivates the surface effectively
- Pilling-Bedworth Ratio (ratio of oxide volume grown to unoxidized material consumed in oxidation) is close to 2, hence oxide stability is good



- GaAs does not have a natural stable oxide
- Oxides of Ga and As create cracking in the interface, leading to more oxidation

Passivation of GaAs

- Strategy: Passivate GaAs surface by tying up surfacial dangling bonds…

But *HOW?*

- form chemical bonds at the surface, and allow for a passivating capping layer by using materials having elements that have an affinity to Ga and/or As

OR

- tie up the bonds in a capless process

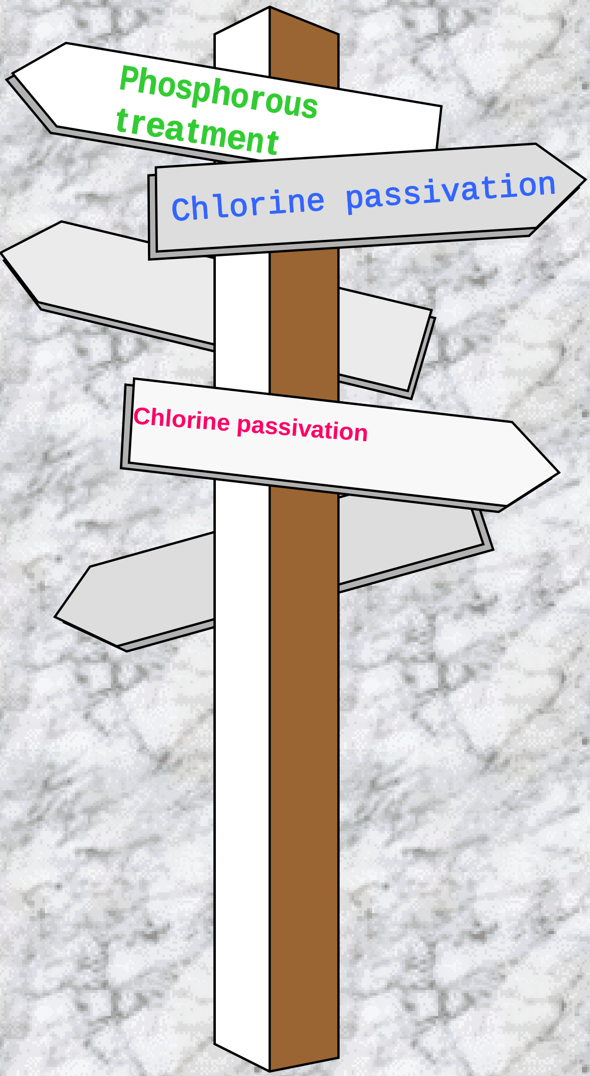
Options for surface passivation of GaAs

- Passivation by a suitable ***capping*** process
  - Thin film deposition by plasma means
    - using poly-thiophene
    - using nanocrystalline ZnSe
  - Thin film deposition by dipping in liquids
    - using ZnS solution
  - Thin film deposition by evaporation
    - using selenium

- ***Capless***, non-contact passivation process
  - using ultrafast laser

Other means of passivation

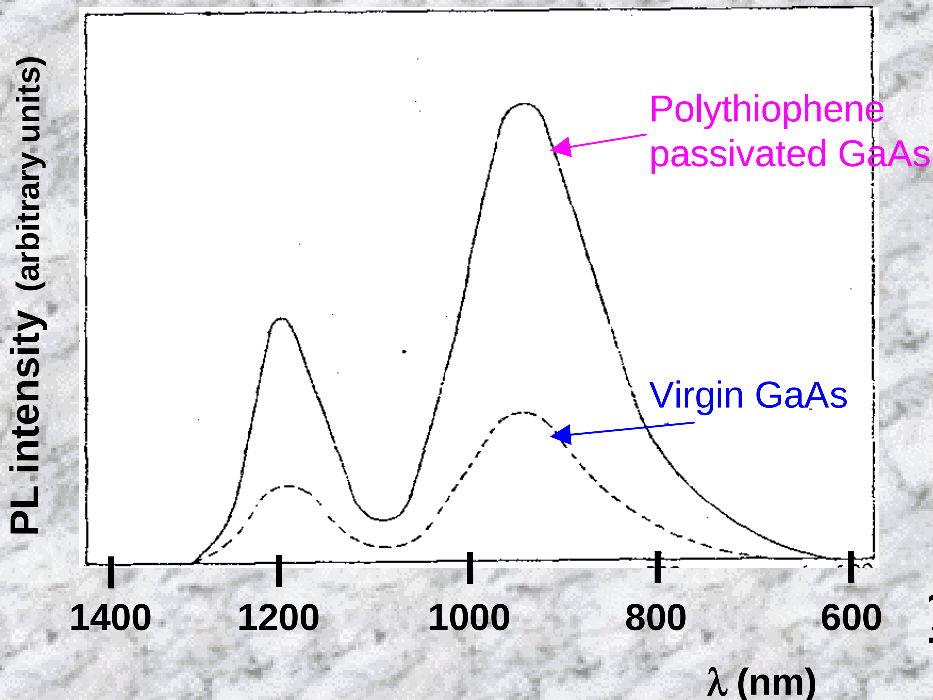
- Chlorine passivation
- Phosphorous treatment
- ..

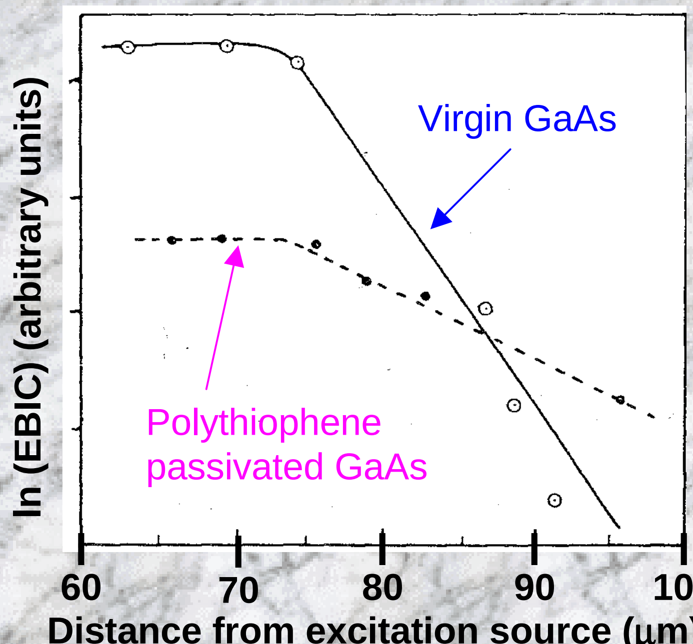


Capping based passivation - Polythiophene

- Polythiophene
  - Heterocyclic polymer containing sulfur
  - Deposited by plasma polymerization
- **Characterization tools used:**
  - Photoluminescence (PL)
  - Electron beam induced current (EBIC)
  - Surface recombination velocity (SRV)
- **Results:**
  - 3X increase in PL intensity (a measure of reduction in defect centers, radiatively recombining)
  - Slower decay of current with distance measured, meaning reduced electronically active defects
  - Lower values of SRV, by a factor of 4, indicating reduction in surface defect density

Results


PL intensity (arbitrary units)
Polythiophene
passivated GaAs
Virgin GaAs
1400
1200
1000
800
600
λ (nm)

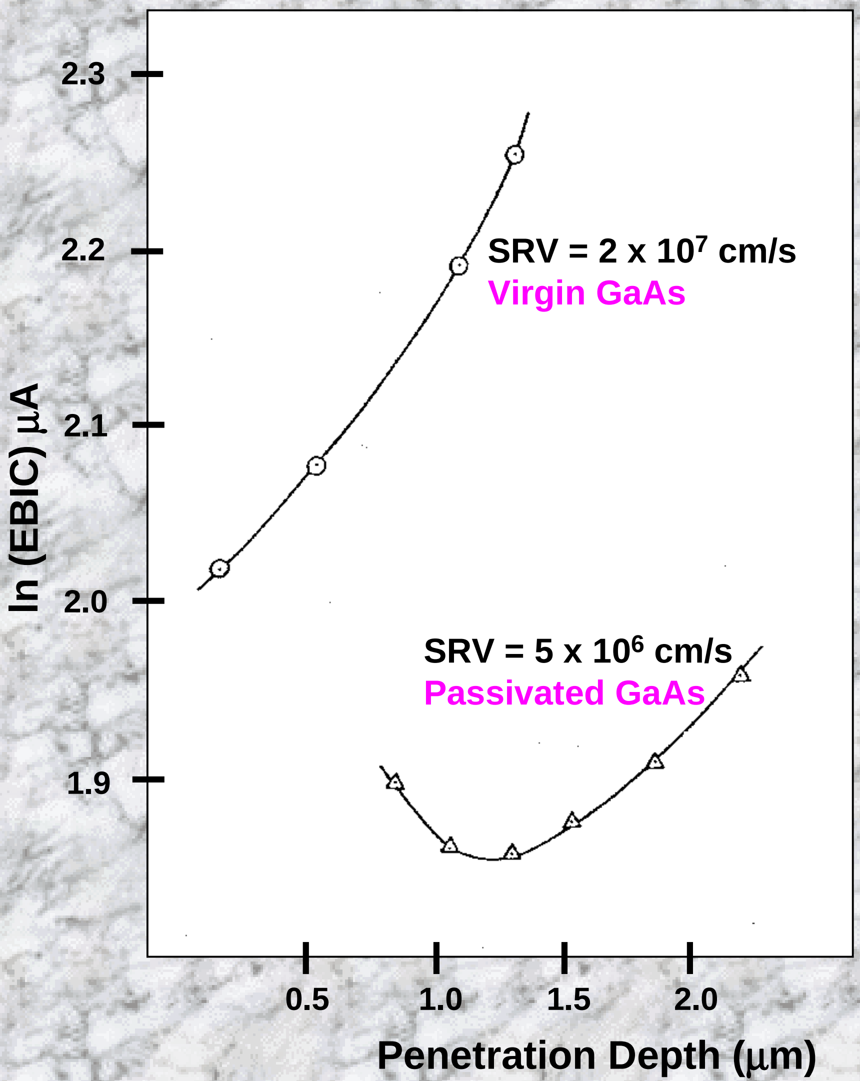

ln (EBIC) (arbitrary units)
Virgin GaAs
Polythiophene
passivated GaAs
60
70
80
90
100
Distance from excitation source (μm)

Results (contd..)

Surface recombination velocity (SRV) describes the rate of loss of charge carriers at the surface of a material. Estimation of SRV involves measurement of EBIC as a function of incident electron beam energies (and hence that of excitation depths). Natural logarithm of the EBIC current 'I' is then plotted against its corresponding penetration depth. The slope of this curve at the surface or the interface, multiplied by the diffusion coefficient of the excess charge carriers D, gives the SRV, '*s*'. Thus,

$$s = D(\ln I)$$

Reduced SRV indicates that passivation with polythiophene reduces concentration of surface defects in GaAs



Capping based passivation - nanocrystalline ZnSe

- Deposited using a solution of sodium selenosulfate in an alkaline media
- Maximum particulate size measured to ~2 μm
- **Characterization tools used:**
  - Photoluminescence (PL)
  - Electron beam induced current (EBIC)
  - Surface recombination velocity (SRV)
- **Results**
  - Over 1000-fold increase in PL intensity after passivation
  - 4-fold reduction in EBIC slope
  - 15-fold reduction in SRV

Capless passivation - use of fs lasers

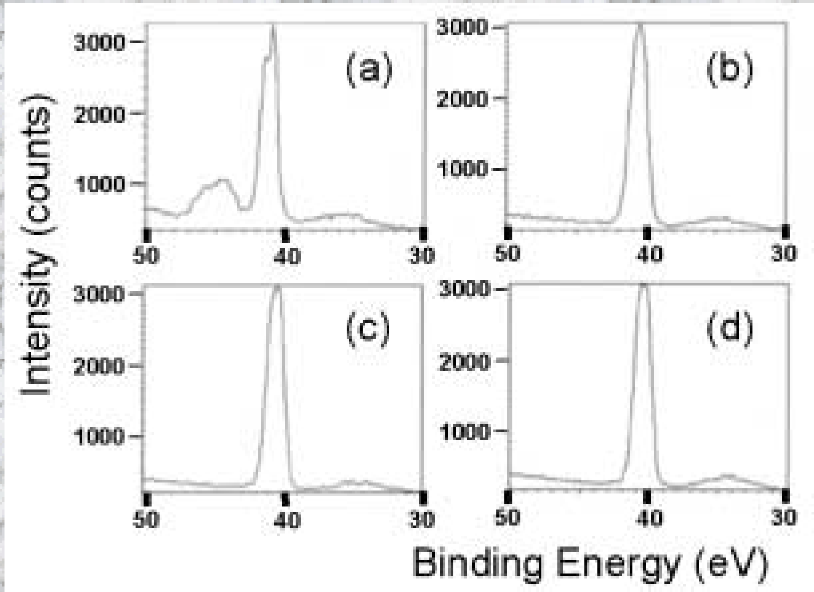
- **Why fs lasers:**
  - Clean, contamination-free and contactless processing technique
  - UV frequencies are absorbed efficiently, making materials processing very effective
  - Absence of heat affected zone (HAZ) makes materials processing, chemically clean and mechanically precise
- **Experimental conditions:**
  - Air ambience
  - Laser wavelength: 248 nm
  - Laser pulse duration: 380 fs
  - Laser pulse energy: 1.3 mJ/cm^2
  - Repetition rate: 3-9 Hz

Characterization techniques used

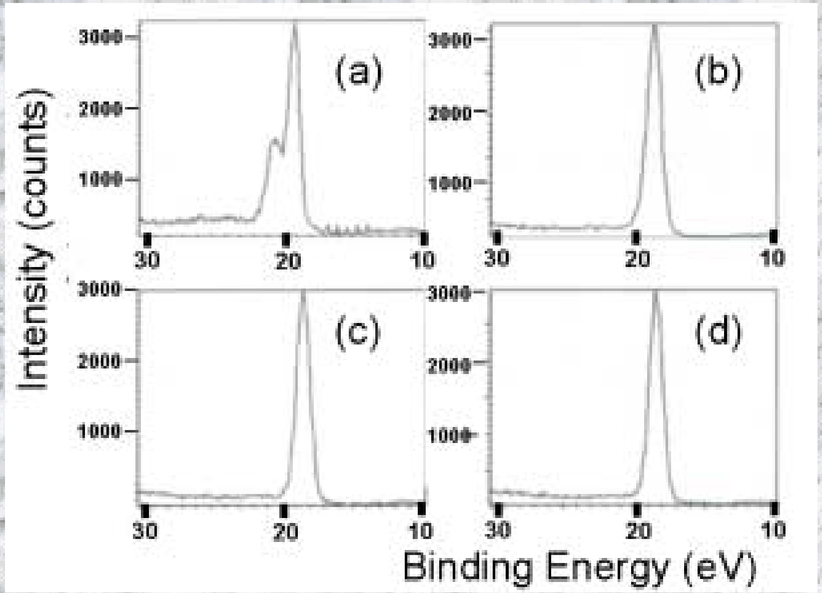
- Fs laser treated GaAs samples were characterized with the following techniques:
  - X-ray photoelectron spectroscopy (XPS) ⇒ for identifying chemical signature of the surface
  - Scanning electron microscopy (SEM) ⇒ for observing surface modifications, if any, on a micoscopic scale
  - Atomic force microscopy (AFM) ⇒ for observing surface modifications, if any, on an atomic scale
  - Thermally stimulated exoelectron emission (TSEE) spectroscopy ⇒ for determining concentration of electronically active surface states

Results

A) XPS results



XPS spectra of As-3d peak: (a) virgin GaAs, (b) fs laser treated-as is, (c) 2 weeks after laser treatment and ambient storage (d) six weeks after fs laser treatment and ambient storage



XPS spectra of Ga-3d peak: (a) virgin GaAs, (b) fs laser treated-as is, (c) 2 weeks after laser treatment and ambient storage (d) six weeks after fs laser treatment and ambient storage

Observations:

(1) Oxide signature absent after passivating treatment.

(2) The oxide peak does not reappear even after storage of treated samples in ambient, for at least up to six weeks.

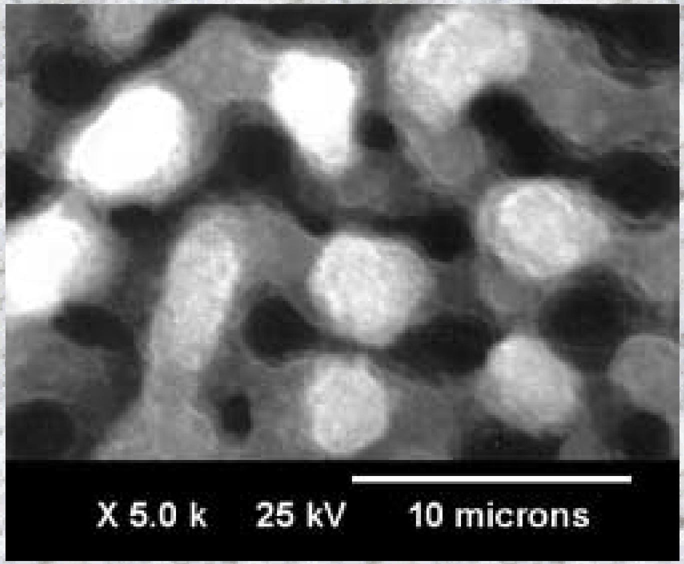
Interpretation:

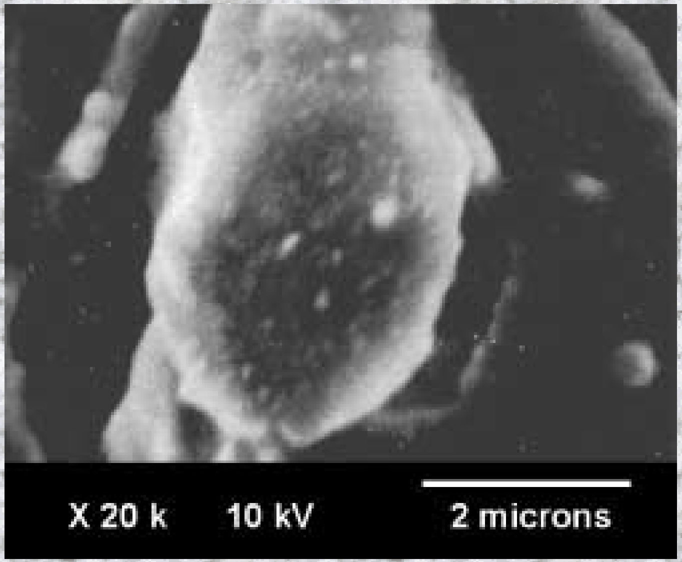
(1) fs laser treatment was successful in passivating the GaAs surface.

(2) The passivating effects were stable, and did not have any special storage requirements.

Results (contd…)

B) SEM analysis



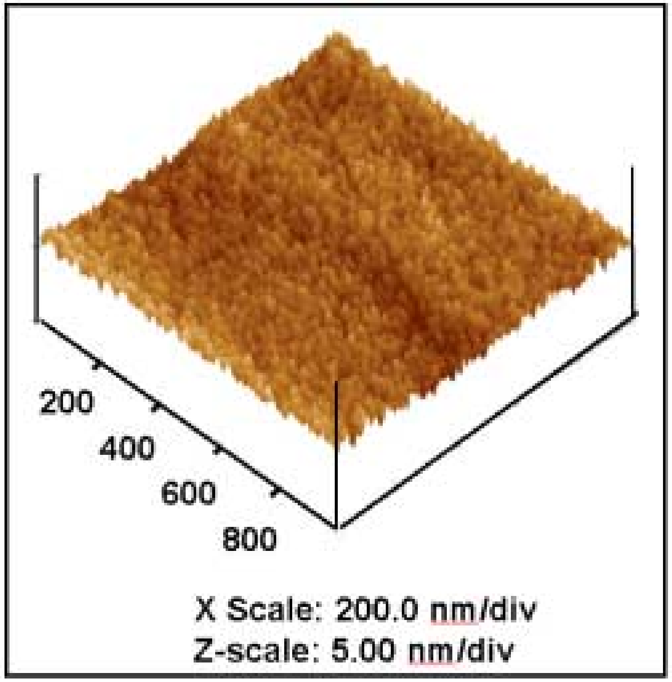


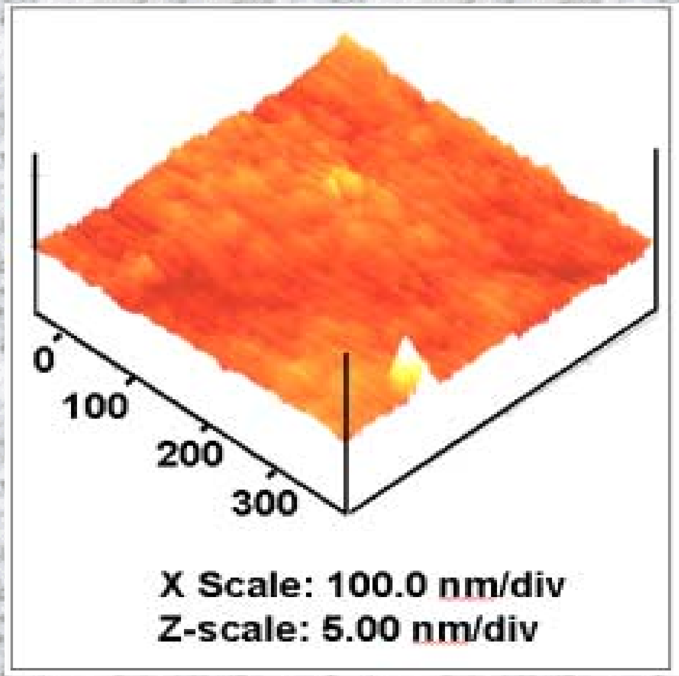
Fs laser treated GaAs samples. Untreated samples did not exhibit such a cluster formation

SEM analysis suggests that passivating effects may have been realized by a bond-tying mechanism at the treated GaAs surface. Such a bond-tying phenomenon may have caused the formation of the observed micro-clusters

Results (contd…)

C) AFM analysis

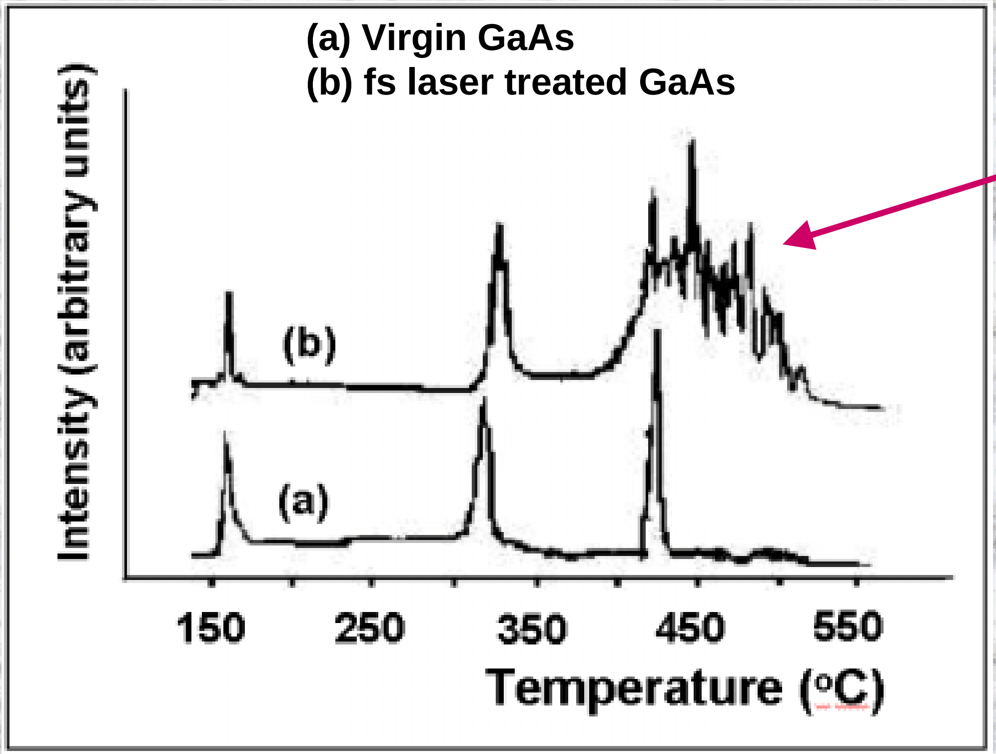




AFM analysis suggests an overall 'smoothening' of the surface, yet formation of micro-clusters

Results (contd…)

D) TSEE analysis



TSEE analysis suggests the presence of micro-clusters at the treated GaAs surface. This was later confirmed by SEM and AFM analysis

Conclusions

- Multiple options were evaluated for passivation of GaAs surface. Each technique generally has certain advantages and some challenges
- An ultrafast laser based processing technique was demonstrated to exhibit excellent passivating effects. *This process is being fine-tuned for potential commercial applications. The technology is protected with a U.S. and an international patent (pending)*
- TSEE was demonstrated as a capable tool for detecting electronically active structural micro-changes, and has demonstrated its strength as a spectroscopic characterization tool.

Contact information:

Dr. Tarak A. Railkar
Conexant Systems Inc.
4311 Jamboree Road MS: E04-401
Newport Beach CA 92660
Tel: 949-483-7062
e-mail: tarak.railkar@conexant.com